

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of

KASZTELAN et al.

Examiner: Christina ILDEBRANDO,

Serial No.: 09/603,838

Group Art Unit: 1725

Filed:10/16/2000

For: CATALYST THAT CONTAINS A ZEOLITE THAT IS HIGH IN AN ELEMENT OF GROUPS VIB AND/OR VIII AND ITS USE IN HYDROREFINING AND HYDROCRACKING OF HYDROCARBONS FRACTIONS.

**DECLARATION UNDER RULE 37 C.F.R. §1.132**

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

I, Slavik KASZTELAN, being duly warned, declare and say as follows:

THAT, I am a French citizen ; that I obtained an Engineer Diploma delivered by "Ecole des Hautes Etudes Industrielles de Lille" (France) in 1982 ; that I was received as a "Docteur Ingénieur" in 1984 and as a "Doctor habilité à diriger des recherches" in 1991 by "Université de Lille" ; and that I know reside in 92500 Rueil-Malmaison, France, 27 Rue Raymond Queneau.

THAT, I was engaged on research by "Institut Français du Pétrole" Rueil-Malmaison (France) in their Kinetics and Catalysis Department in 1988, where I was continuously and actively in charge of researches in the fields of hydrocracking, hydroisomerization, dewaxing and hydrogenation of aromatic compounds; that from January 1995 to March 2001, I was Project Manager in the fields of "fundamental research in heterogeneous catalysis" and then of "hydrotreatment catalysts" ; and that since then I have been Manager of the Kinetics and Catalysis Research Division.

THAT, I am familiar with the processes and catalysts for hydrocracking.

THAT, I have supervised the following examples :

**Example10 : Production of Catalyst G not in Accordance to Procedure**

Catalyst G is prepared in the following way : in a first step, a Y zeolite powder with a crystalline parameter that is equal to 2.429 nm and an overall Si/Al atomic ratio of 13.6 and an Si/Al framework atomic ratio of 19 is prepared. This zeolite is ion-exchanged with a solution of nickel nitrate such as to deposit 11% NiO by weight with respect to the zeolite. The solid is then dried for one night at 120°C under air, and finally it is calcined for two hours under dry air at 500°C. Considering the method of preparation, nickel is located in the porous network of the zeolite.

Solid II of type MoP / alumina is then prepared by impregnation in the dry state of SB3-type alumina provided by the Condéa Compagny i.e., by filling the pore volume by an aqueous solution of a mixture of ammonium heptamolybdate and orthophosphoric acid. After impregnation the solid is then dried for one night at 120°C under air. The composition of the impregnation solution is calculated to obtain on the final solid II 15.4 % by weight of molybdenum oxide  $\text{MoO}_3$ , 5.5% by weight of phosphorus oxide  $\text{P}_2\text{O}_5$  and 80.1 % by weight of alumina  $\text{Al}_2\text{O}_3$ .

To obtain catalyst G, 18.4 g of solid I and 81.6 g of solid II under a powder form are comulled. The mixed paste is then extruded through a die with a 1.4 mm diameter. The extrudates are then dried for one night at 120°C under air and then calcined at 500°C under air. The final catalyst G contains 2.02% by weight of nickel oxide NiO, 12.5% by weight of molybdenum oxide  $\text{MoO}_3$ , 4.48% by weight of phosphorus oxide  $\text{P}_2\text{O}_5$  and 16.4% by weight of Y zeolite.

**Example 11 : Production of Catalyst H not in Accordance to Procedure**

Catalyst H is prepared in the following way : in a first step, a Y zeolite powder with a crystalline parameter that is equal to 2.429 nm and an overall Si/Al atomic ratio of 13.6 and an Si/Al framework atomic ratio of 19 is prepared. This zeolite is ion-exchanged with a solution of nickel nitrate such as to deposit 2.3% NiO by weight with respect to the zeolite. The solid is then dried for one night at 120°C under air, and finally it is calcined for two hours under dry air at 500°C. Solid III of type Ni / zeolite is obtained. Considering the method of preparation, nickel is located in the porous network of the zeolite.

Solid IV of type MoP on alumina is then prepared by impregnation in the dry state of SB3-type alumina provided by the Condéa Compagny i.e., by filling the pore volume by an aqueous solution of a mixture of ammonium heptamolybdate and orthophosphoric acid. After impregnation the solid is then dried for one night at 120°C under air. The composition of the impregnation solution is calculated to obtain on the final solid IV 20.8 % by weight of molybdenum oxide  $\text{MoO}_3$ , 7.3% by weight of phosphorus oxide  $\text{P}_2\text{O}_5$  and 72.05 % by weight of alumina  $\text{Al}_2\text{O}_3$ .

To obtain catalyst H, 62 g of solid III and 38 g of solid IV under a powder form are comilled. The mixed paste is then extruded through a die with a 1.4 mm diameter. The extrudates are then dried for one night at 120°C under air and then calcined at 500°C under air. The final catalyst H contains 1.43% by weight of nickel oxide NiO, 7.9% by weight of molybdenum oxide  $\text{MoO}_3$ , 2.71% by weight of phosphorus oxide  $\text{P}_2\text{O}_5$  and 60.6% by weight of Y zeolite.

**Example 12 : Comparison of Catalysts C, D, G and H for Hydrocracking of a Vacuum Distillate with Moderate Pressure.**

The Catalysts G and H whose preparations are described in the examples 10 and 11 are tested under the conditions of hydrocracking at moderate pressure as described in the example 5 with the same petroleum feedstock. The characteristics of catalysts G and H,

their activity, gross conversion CB at 400°C, coarse selectivity SB, hydrodesulfurization conversion HDS and hydrodenitrating conversion HDN are compared in the following table with those obtained for catalysts C and D.

	C	D	E	F
Zeolite (%)	16.2	60.4	16.4	60.6
NiO (%)	2.2	1.5	2.02	1.43
MoO <sub>3</sub> (%) on alumina	12.3	7.3	12.5	7.9
P <sub>2</sub> O <sub>5</sub> (%)	4.4	2.5	4.48	2.71
MoO <sub>3</sub> in zeolite (% by weight of zeolite)	2.4	2.4	0	0
NiO in zeolite (% by weight of zeolite)	0	0	11	2.3
CB (% by weight)	49.3	56.9	46.2	55.0
SB	82.0	79.9	80.1	78.4
HDS (%)	99.6	99.7	99.2	97.2
HDN (%)	97.8	98.9	97.0	92.3

For a same amount of zeolite, oxide matrix, hydrogenating element and phosphorous, it is observed that the catalyst containing molybdenum in the porous network of the zeolite (catalyst C) provides better conversion levels of fraction 380°C<sup>plus</sup> than catalyst G containing Ni in the porous network. Selectivity, HDS and HDN activities are also worse for catalyst G.

The improvement of the conversion, the selectivity and the HDS and HDN activities due to the presence of molybdenum in the porous network of the zeolite is more marked when catalyst contains a large amount of zeolite. The comparison of catalysts H and D shows that catalyst H provides worse conversion, selectivity and HDS and HDN activities than D catalyst.

This lack of activity and selectivity of G and H catalysts containing Ni in the porous network of the zeolite shows that use of this type of catalyst is not advantageous. This may be due to a weaker synergy between Ni and Mo for this type of solid.

**Example13 : Comparison of Catalysts C, D, G and H for Hydrocracking of a Vacuum Distillate with Higher Pressure.**

The Catalysts G and H whose preparations are described in examples 10 and 11 are tested under the conditions of hydrocracking at high pressure (12 MPa) as described in example 6 with the same petroleum feedstock.

In the following table, the reaction temperature for 70% gross conversion and the coarse selectivity for catalysts G and H are compared with those obtained for catalysts C and D.

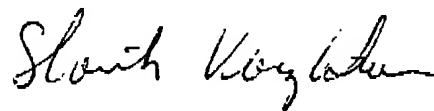
	T (°C) for 70% Gross Conversion	SB
C	384	67
D	365	64
G	386	62
H	369	50

The comparison of catalysts C with D and G with H shows that by increasing the amount of zeolite, the activity of the catalyst that is indicated by the temperature level required to obtain 70% of conversion of the feedstock is considerably increased. In the case where nickel is located in the porous network of the zeolite, this increase of activity leads to a significant loss of selectivity (catalysts G and H) with respect to catalysts C and D.

In short, catalysts containing nickel in the porous network of the zeolite are less active and less selective than catalysts that contain molybdenum in the porous network of the zeolite.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 Title 18 of United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Rueil-Malmaison, December 19, 2002



Slavik KASZTELAN